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methyl phenyliminomalonate

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CONDENSATION REACTIONS WITH METHYL
PHENYLIMINOMALONATE

BY

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THESIS FOR THE DEGREE OF BACHELOR OF SCIENCE

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ENTITLED *Condensation Reactions*
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IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

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in Chemistry

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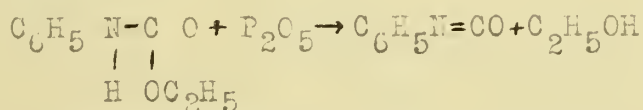
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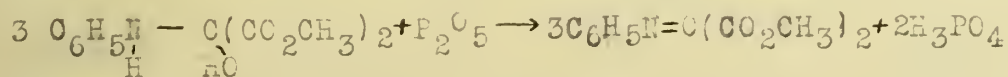


CONDENSATION REACTIONS WITH METHYL PHENYLIMINOMALONATE

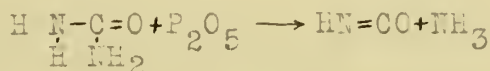
Methyl phenyliminomalonnate⁽¹⁾, $C_6H_5N=C(CO_2CH_3)_2$, is prepared by dehydrating methyl anilinetartronnate, $C_6H_5NH-C(CO_2CH_3)_2$, by means of phosphorus pentoxide. As will readily be seen, it has a striking resemblance to ^{phenyl}isocyanate. The most reactive point is the double bond between the nitrogen and the carbon. According to theory, compounds with easily dissociable hydrogen should be added readily at this point. The modes of formation and many reactions of phenyl isocyanate and phenyliminomalonnate are also similar. The former is made by treating phenyl urethane with phosphorus pentoxide and removing the elements of alcohol:



The latter is made by treating methyl anilinetartronnate with phosphorus pentoxide and removing the elements of water:



Cyanic acid, also, may be prepared by treating urea with phosphorus pentoxide and removing the elements of ammonia:



The chief product in this case is cyanic acid, though the reaction

(1) J. Am. Chem. Soc. 31, 1057.

Spenser, Thesis U of I. 1909.



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is more complicated than appears from the equation.

When dry hydrochloric acid gas is passed into phenyl isocyanate, heat is generated, and on cooling, a solid crystalline mass is formed. According to Hentschel⁽¹⁾, the compound thus formed has the formula $C_6H_5N=CCl$. He does not state specifically that the hydrogen is added to the nitrogen and the chlorine to the carbon, thus:

$C_6H_5\overset{H}{\underset{Cl}{N}}-CO$. The attempt was made to prepare a similar compound from methyl phenyliminomalonate and hydrochloric acid gas, having the formula $C_6H_5\overset{H}{\underset{Cl}{N}}-C(CO_2CH_3)_2$. A solid white substance was obtained, which decomposed so rapidly that it could not be purified, nor could it be handled in the air.

In his work on phenyl isocyanate, Hofmann⁽²⁾ found that it easily added ammonia and its derivatives on the double bond to form substituted ureas. $C_6H_5N=CCl + NH_3 \rightarrow C_6H_5\overset{NH_2}{\underset{NH_2}{N}}-CO$

A great variety of compounds can thus be made. The action of ammonia on methyl phenyliminomalonate was tested.

$C_6H_5N=C(CO_2CH_3)_2 + NH_3 \rightarrow C_6H_5\overset{H_2N}{\underset{H_2N}{N}}-C(CO_2CH_3)_2$
A colorless, crystalline product was obtained. The yield was small and the product rapidly decomposed, giving off ammonia and forming a polymerization gum.

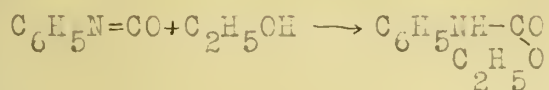
Gumpert⁽³⁾ found that phenyl isocyanate treated with phenol yields phenyl carbamine phenyl ether: $C_6H_5N=CCl + C_6H_5CH \rightarrow C_6H_5\overset{NH-C_6H_5}{\underset{C_6H_5}{N}}-CO$

(1) Hentschel B.18, 1178.

(2) Hofmann B. 3, 655.

(3) Gumpert - J.Prakt. Chem.(2) 32, 281.

The reaction begins at ordinary temperatures but must be carried to completion on the water bath. A crystalline compound is obtained. Alcohols and phenyl isocyanate yield carbanilic esters.



A similar reaction was tried with ethyl alcohol and methyl phenyliminomalonate. Beautiful colorless crystals of methyl anilinoethoxymalonate, $\text{C}_6\text{H}_5\text{NH}-\underset{\text{C}_2\text{H}_5}{\underset{\text{O}}{\text{C}}}(\text{CO}_2\text{CH}_3)_2$ were obtained. A study of the action of hydrochloric acid on methyl anilinetartronate was made. Conrad and Reinbach⁽¹⁾ prepared the hydrochloride of methyl anilinomalonnate which was not very stable in the air. When hydrochloric acid gas was passed into an ethereal solution of methyl anilinetartronate, an unstable white compound was obtained, similar to the hydrochloride of methyl anilinomalonnate.

EXPERIMENTAL

Preparation of Methyl Anilinetartronate.

The methyl oxomalonate used in this preparation was made in the usual way as described by Curtiss and Spenser⁽²⁾. The calculated amount of aniline, diluted with an equal volume of dry ether, was added drop by drop to this substance, keeping the temperature below zero in a freezing mixture. If the aniline is not added in a dilute condition, the product is a mixture of dianilino malonnate $(\text{C}_6\text{H}_5\text{NH})_2\text{C}(\text{CO}_2\text{C}_2\text{H}_5)_2$, and dihydroxymalonate $(\text{HO})_2\text{C}(\text{CO}_2\text{CH}_3)_2$, as

(1)

Conrad & Reinbach - 35, 512.

(2)

Curtiss & Spenser - J. M. Chem. Soc. 31, 1054. Spenser - Thesis - U. of I., 1909.

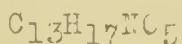
noted by Curtiss and Spenser(1). The product soon went solid and it was then washed with ether and recrystallized from the same solvent. It formed small, glistening needles, having a melting point of 102°C. Viewed under the microscope these needles appeared cylindrical, but they were probably prismatic in shape.

Action of Ethyl Alcohol on Methyl Phenyliminomalonate

The phenyliminomalonate was prepared by thoroughly mixing one mol of the anilino tartronate with one and one-half mols of phosphorus pentoxide(2). Most of the yellow oil which separated could be decanted, and the remainder could be extracted with ether. The yellow color of this compound can be explained by the theory of isomerism of Bal, and Desch(3).

The rapid interchange of the linking of the carbonyl groups with the N=O group as shown here, causes ether vibrations of such a nature as to produce the color of the phenyliminomalonate.

2.35 g. of methyl phenyliminomalonate (1 mol) were treated with 0.49 g. (1 mol) of absolute ethyl alcohol. There was a slight evolution of heat, but the substance did not crystallize until the next day. The substance was washed and recrystallized from alcohol and melted at 88°C (uncorr.). It is easily soluble in ether, benzene, chloroform, and carbon tetrachloride; fairly soluble in alcohol; and difficultly soluble in ligroin. It turns yellow when kept over sulphuric acid.



	C	H	N
Calculated	58.42	6.36	5.24
Found	58.65	6.39	5.17

(1) See note 2, page 3.

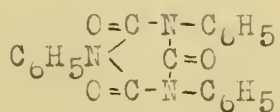
(2) Curtiss & Spenser - J. Am. Chem. Soc. 31, 1057; Spenser, Thesis - U. of I 1909.

(3) Bal & Desch - J. Chem. Soc. 87, 706.

Action of Ammonia on Methyl Phenyliminomalonate

Dry ammonia was passed into an ethereal solution of methyl phenyliminomalonate, and the time was varied in different tests from thirty seconds to thirty-five minutes. A very slight precipitate formed at once. After standing over night, a yellow powder settled out. This was insoluble in all organic solvents and could not be purified. It was not crystalline but seemed rather resinous in character, and was probably a polymerization product. When the gas was passed in slowly for about thirty seconds at a time and the effect noted after each passage of the gas, a white, crystalline, prismatic product was obtained. The yield was about ten percent of the theoretical amount, and the substance decomposed in a very short time, giving off ammonia when kept in a stoppered tube.

Benzene was also used as a solvent and the gas was passed in for three minutes. The benzene was then evaporated in a vacuum desiccator. This required several hours. A thick yellow oil was left, which, when diluted with ether, formed a yellow solution with the simultaneous separation of a white flocculent precipitate. The white substance was filtered off. It was not stable and turned to a brown sticky mass at once on the filter, giving off ammonia. It is likely that methyl aminocanilinomalonate $C_6H_5NH_2 \cdot C(CO_2CH_3)_2$, is first formed as an addition product and that this, being very unstable, loses ammonia at once in the air, and that the resulting nascent phenyliminomalonate polymerizes, as does its analogue, phenyl isocyanate to give cyanuric acid



Tests were made of the action of hydrochloric acid gas on phenyliminomalonate dissolved in ether. The gas was passed in for fifteen to thirty minutes keeping the solution below 0°C., but no precipitate formed. On evaporating the ether a sticky solid remained, but this could not be purified nor could it be handled in the air without rapid decomposition.

Action of Hydrochloric Acid Gas on Methyl Anilinetartronate

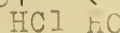
A half gram of anilinetartronate was dissolved in 15 c.c. of dry ether, and dry hydrochloric acid gas was passed in for four or five minutes until no further precipitate formed. Then the flask was put into a dessicator and evacuated. The ether was evaporated and the product weighed. The increase in weight indicated an addition of two mols of hydrochloric acid gas:

Calculated (for 2 mols)	22.72 % Cl	
Found	20.09 %	20.48 %

Part of the substance was dissolved in water which dissociates the hydrochloric acid from the compound. The organic matter was extracted with ether. The ether extract was tested for chlorine but none was found. The chlorine in the aqueous solution was precipitated with silver nitrate and the analyses showed only one mol of hydrochloric acid added:

Calculated (for 1 mol)	12.86 %	
Found	13.14 %	- 12.59 %

The substance was a white powder which decomposed rapidly in the air, giving off hydrochloric acid. It seems more probable that only one mol of hydrochloric acid is added. The analysis should have been made by Carius' method, but this was omitted for want of time. The compound formed is probably $\text{C}_6\text{H}_5\text{NH}-\text{C}(\text{CO}_2\text{CH}_3)_2$.



Owing to the ease with which this substance decomposed it could not be purified, nor could it be well characterized.





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